

Improved reproducibility of BET specific surface area by AFSM (Advanced Free Space Measurement)

BELSORP instruments

The gas sorption isotherm (ísos ,equal' and thérme ,heat') is measured at a specific temperature. Commonly liquid refrigerants (e. g. liquid nitrogen, short LN₂) are used to keep the temperature constant, 77 K in case of nitrogen (boiling point). The liquid nitrogen in the Dewar vessel vaporizes during the adsorption measurement, and the level of the liquid decreases gradually.

In the volumetric system the adsorbed amount is calculated from the pressure change before and after adsorption based on the ideal gas equation. A certain amount of gas with pressure p_i is filled into manifold with known volume V_s . The valve to the sample port is opened and the pressure after reaching equilibrium p_e is measured.

$$N = n_1 - n_2 = [(p_i - p_e) V_s - p_e V_d] / RT$$

N = adsorbed amount of substance
 n_1 = amount of gas at pressure p_i
 n_2 = amount of gas at pressure p_e
 p_i = initial pressure (before adsorption)
 p_e = equilibrium pressure (after adsorption)
 V_s = geometric volume of manifold
 V_d = dead volume
 R = universal gas constant 8.314 J/mol K
 T = temperature

From the pressure difference p_i and p_e and the dead volume V_d the adsorbed amount can be calculated. The dead volume in the sample cell changes gradually along with this level of refrigerant. However, there are two options to consider the dead volume during measurement. The dead volume is determined at the beginning or at the end of the measurement and is tried to keep constant during the whole measurement.

Our patented AFSM™ (Advanced Free Space Measurement) determines an initial dead volume of the sample cell and an initial dead volume of a reference cell at the same time.¹

¹AFSM™; US Patent: 6.595.036

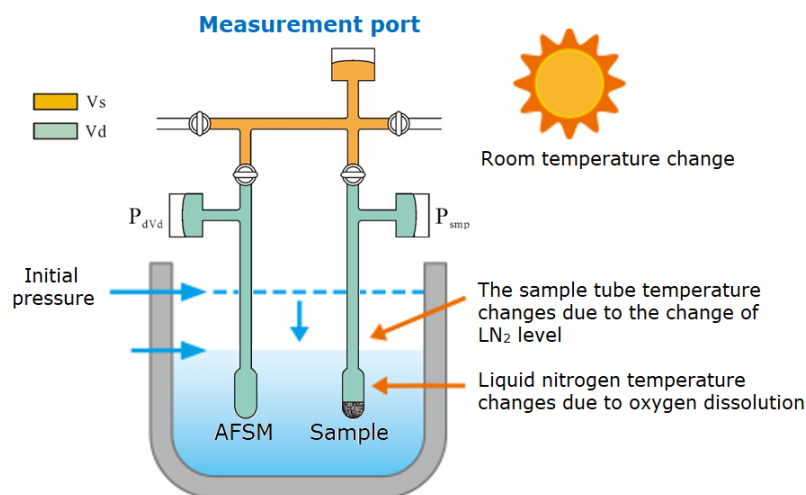


Fig. 1 Adsorption isotherm measurements using LN₂ and LAr by AFSM

Since the change of the dead volume in the sample and reference cell is equal, the dead volume change is continuously followed via the reference cell. Therefore, AFSMTM enables to calculate the adsorbed quantity based on the measured dead volume at any time during measurement without keeping the liquid level of the refrigerant constant during the whole measurement (see Fig. 1). Changes in room temperature during measurement and changes in liquid nitrogen temperature due to oxygen dissolution can be considered, enabling accurate and highly reproducible adsorption quantity evaluation. The change of dead volume in the sample cell is expressed by following equation:

$$dV_d = [1 - (p_i/p_e)] * V_{d,ref}$$

$$V_{d,sample} = V_{d,ini} - dV_d$$

dV_d = Free space change
 $V_{d,ref}$ = dead volume of reference cell
 $V_{d,sample}$ = dead volume of sample cell
 $V_{d,ini}$ = initial dead volume of sample cell

Figure 2 shows a graph with the total surface area on the horizontal axis and reproducibility on the vertical axis for three exemplary materials with different surface areas.

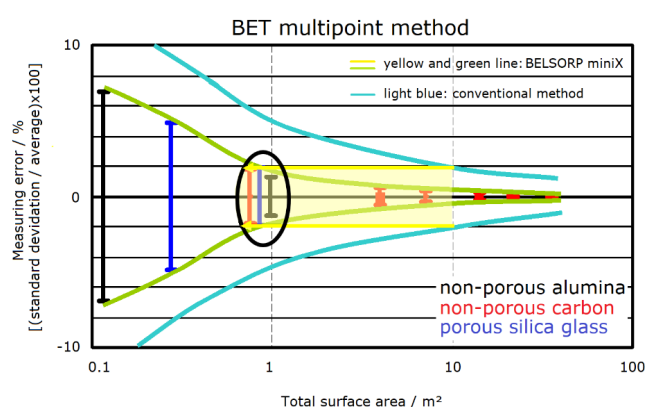


Fig. 2 Reproducibility of BET surface area of non-porous alumina, non-porous carbon, and porous silica

The comparison between the conventional method (keeping VD constant; light blue) and AFSM (continuously measuring VD; green) shows that AFSM is more reproducible in the whole surface area range, especially for smaller BET surface areas. With AFSM it is possible to measure low total surfaces down of 1 m² with a reproducibility of $\pm 2\%$, while conventional methods are limited to 10 m² with similar reproducibility. Summarized, the sensitivity is improved by 10 times by AFSM.